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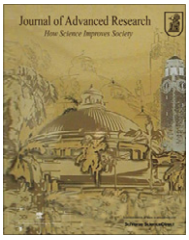

ORIGINAL ARTICLE

Isotope effects of neodymium in different ligands exchange systems studied by ion exchange displacement chromatography

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KEYWORDS

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Abstract The isotope effects of neodymium in Nd-glycolate ligand exchange system were studied by using ion exchange chromatography. The separation coefficients of neodymium isotopes, ε's, were calculated from the observed isotopic ratios at the front and rear boundaries of the neodymium adsorption band. The values of separation coefficients of neodymium isotopes, ε's, for the Nd-glycolate ligand exchange system were compared with those of Nd-malate and Nd-citrate, which indicated that the isotope effects of neodymium as studied by the three ligands takes the following direction Malate > Citrate > Glycolate. This order agrees with the number of available sites for complexation of each ligand. The values of the plate height, HETP of Nd in Nd-ligand exchange systems were also calculated.

Introduction

The research reports, accumulated since the fortieth of the last century, regarding the isotope effects in chemical exchange system proved that there are little differences in the chemical properties of the different isotopes of the same element. Recently, researches in the isotopes separation field indicated that the isotopes of a given element may show some quantitative differences in chemical reaction equilibria and/or reaction rates; the former is the equilibrium isotope effects and the later is the kinetic isotope effects. Separation of isotopes by ion exchange chromatography is one of the most effective chemical exchange methods, which is based on the chemical equilibrium between isotopic species distributed between the stationary resin phase and the mobile solution phase [1]. It has been applied successfully to the separation of isotopes of various elements in ligand exchange systems, in particular, those using hydroxycarboxylates as ligands, such as Ce [1], Gd [2], Zn

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[3,4], Eu [5,6], Cu [7,8] and Nd [9–11] and in electron exchange systems such as Eu [12,13] and U [14,15].

The first trial to explore the origin of the isotope effects in chemical exchange reactions was carried out by Clewett and Schaap [16], who suggested that the isotope effects in a chemical exchange reaction are due to a slight difference in the affinity of the isotopes for a given molecule or complex due to minor variances in the internal energies, mainly vibrational energy, of the molecule. Based on the quantum molecular vibration energy, Bigeleisen formulated the method to calculate the isotope exchange equilibrium constant from spectroscopic data [17]. This method was used to calculate the equilibrium constant of the isotopic exchange of many elements ranging from hydrogen to uranium. Unfortunately, this method could not explain the anomalous isotope effects of the odd isotopes ^{233}U [15] and ^{235}U [14] among the other uranium even isotopes. This anomaly was found to be similar to the odd–even staggering of the isotope shift in the atomic spectra. According to the new theory derived by Bigeleisen, this anomaly is believed to be due to the field shift [18]. Later on, similar odd–even isotope effects were found in Gd [2], Zn [3,4,19–21], Nd [9–11] and Cd [22].

Lanthanides and actinides are known to have deformed nuclei, which cause the charge distribution effects in the isotope shifts of the atomic emission spectral lines. Therefore, the field shift is expected to have a great effect on their isotope effects. In case of Cd, The contribution of the nuclear field shift effect to the observed isotope enrichment factor was estimated to be 5–30% [22]. Another supporting proof for the importance of the field shift on isotope effects was given by the study of temperature effect on Eu isotope effects. It was shown that the separation coefficient of Eu isotopes increases with the increase in temperature, which could be explained by the field shift effects [13].

Kim et al. studied the isotope effects of uranyl complexes by means of ion exchange chromatography and reported that the malic acid eluent system had the largest separation coefficient among some selected uranyl carboxylate complexes [23]. Therefore, the purpose of the work is to study the isotope effects of neodymium in ligand exchange system using glycolic, malic and citric acids as mono, di and tri carboxylic acid to compare the effect of different ligands on the isotope effects of Nd in Nd-Ligand exchange system. It is aimed to find the most suitable ligand that gives the highest separation coefficient and to get more information that may lead to more understanding of the theory of isotope effects.

Experimental

Ion exchange resins and reagents

The cation exchange resin used in the ligand exchange system, LXS, was a macroporous strongly acidic cation exchange resin, (SQS, 100–200 Mesh size) obtained as a gift from Asahi chemical Co. Japan, Nd_2O_3 of purity 99.99% was supplied by Alfa-Aesar, USA, and converted to $NdCl_3$ by dissolving in 2 M HCl solution followed by well gentle evaporation, drying the obtained solid salt, washing several times with distilled water followed by evaporation till neutrality, then used without further purification. All other reagents used were of analytical grade and employed without further purification.

Chromatographic system

Neodymium isotope separation experiment based on the ligand complex formation was carried out with a cyclic displacement chromatography system which is composed of three glass columns, 0.8 cm I.D. × 100 cm long, with water jacket, connected in series with Teflon tubes, 1 mm inner diameter, so that they were repeatedly used in merry-go-round way for the desired migration length. The set of apparatus for the chromatographic experiment is illustrated in Fig. 1, while the experimental conditions are summarized in Table 1.

These columns were packed uniformly with the above-mentioned resin. The resin was pretreated with 2 M, mol/dm^3, HCl solution to remove impurities and to convert the resin into H^+ form. This was followed by passing a solution of 0.1 M $CuCl_2$ to convert the resin into Cu^{2+} form. Then a 0.05 M $NdCl_3$ solution was fed into the first column at a constant flow rate by a peristaltic pump to form Nd^{3+} adsorption band. When the Nd^{3+} ion adsorption band had grown to an appropriate length, the supply of the feed solution was stopped. The Nd^{3+} and Cu^{2+} adsorption bands were eluted by an eluent solution containing 0.2 M ammonium malate or 0.15 M ammonium citrate or 0.2 M ammonium glycolate + 0.1 M NH_4NO_3 + 0.0002-NaN_2 adjusted to pH 4.6 with NH_4OH solution. The adsorption band of Nd^{3+} was visible, pink, in contrast with the preceding green Cu band. When the Nd^{3+} adsorption band migration length reached to the desired length, it was eluted out from the last column. The effluent was collected in small fractions that were, thereafter, subjected to the concentration analysis and the isotopic analysis. The temperatures of the columns were kept constant at 25 ± 0.2 °C by circulating the thermostated water through the water jackets surrounding the columns.

Analysis

The concentration of neodymium was determined in each sample by using UV–visible spectrophotometer. The UV–visible

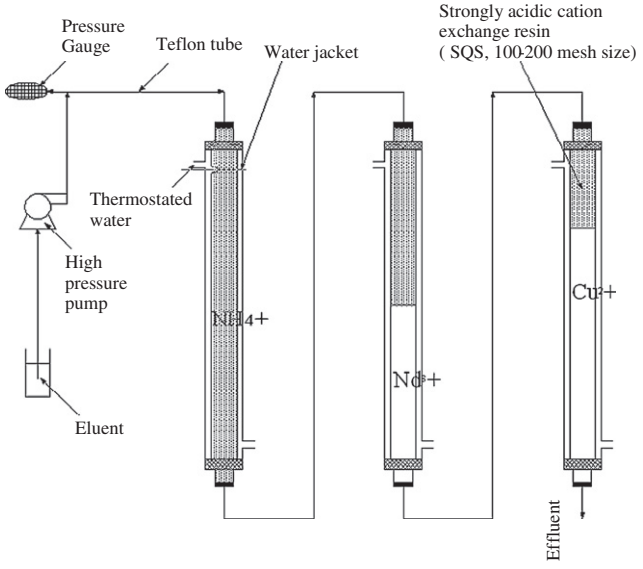

Fig. 1 Schematic diagram of the column setup used for Nd isotope separation by ion exchange chromatography.

Table 1 Experimental conditions of the ligand exchange system of neodymium using different ligands.

Ligands	Malic acid	Citric acid	Glycolic acid
Resin	Strongly cation exchange resin (SQS, 100–200 Mesh size)		
Column size	0.8 cm I.D. and 100 cm length		
Temperature (°C)	25 °C		
pH	4.6		
Pretreatment	2 M HCl followed by 0.1 M $CuCl_2$ to convert resin to Cu^{2+} form		
Feed Solution	0.05 M $NdCl_3$		
Eluent	(0.2 M ammonium malate or 0.15 M ammonium citrate or 0.2 M ammonium glycolate) + 0.1 M NH_4NO_3 + 0.0002NaN_2		
Nd-Band length (cm)	41.0	48.0	42.0
Migration length (cm)	1158.0	1264.0	1158.0
Flow rate (cm^3/min)	0.18	0.183	0.188
Band velocity (cm min^{-1})	0.076	0.072	0.07
Total experiment period (d)	12.1	13.9	13.1
Total effluent volume (cm^3)	2463.0	3210.0	4600.0

spectra of lanthanides were scanned starting from a wavelength of 500 nm by means of UV–visible spectrophotometer to check the interference with any possible other rare earth ions. The intense pink color solution of Nd is the bases for the determination of Nd concentration by photometry after dilution with 0.1 M HCl at wavelength 576 nm. The neodymium isotopic ratios of some selected samples were measured by using a Joel high-resolution inductively coupled plasma mass spectrometer (JMS-plasma ×2). The samples were first burned completely to remove any residues for the carboxylic acids, then dissolved in nitric acid. The samples in the form of $Nd(NO_3)_3$ were supplied to the inlet system which consists of the peristatic sample inlet section of the ICP-MS.

Results and discussion

Chromatographic system

The isotopes separation of certain element by ion exchange chromatography is best achieved by the band displacement technique. This operation is characterized by sandwiching a band of the ions of the element to be studied, Nd^{3+}, between two other chemical species bands, Cu^{2+} and NH_4^+, maintaining self-sharpening band boundaries at both the migration band ends. During this operation, the band of the isotopic chemical species of the element to be separated is eluted through the column by a displacing eluent solution. The velocity of the band displacement is controlled by the eluent type and concentration in the solution phase, equilibrium between the solution phase and the resin phase as well as by the flow rate of the solution.

The profiles of Nd concentration in the effluent fractions, which correspond to the Nd band profile in the column, after 11.58 m migration is shown in Fig. 2 for glycolate system. The sharp boundaries of the band shown in this figure indicate that the chromatographic displacement was almost ideal at both boundaries.

Naturally occurring neodymium is composed of seven isotopes. Abundance's of these isotopes are shown in Table 2. Fig. 3 shows the isotope distribution ratios for neodymium in Nd- glycolate system at constant temperature of 25 °C. The dashed line represents the natural ratio based on current analysis. It can be seen that the heavier isotopes ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd and ^{150}Nd are enriched into the front part, or preferentially fractionated in the complex form in the solution phase. The degree of fractionation of neodymium isotopes takes the order; ^{150}Nd $^{143}Nd \leq {}^{144}Nd \leq {}^{145}Nd \leq {}^{146}Nd \leq {}^{148}Nd \leq$. This tendency is the same as that observed in the chromatographic isotope separation of Ce [1], Gd [2], Zn [3,4], Cu [7,8] and Eu [5,6]. Since the heavier isotope is enriched in the complex species, the observed isotopic enrichment tendency accords with the theoretically expected direction of the isotopic effects in chemical exchange.

The schematic diagram of the expected ion exchange mechanism under the above mentioned conditions, in the simplest form, is represented in Fig. 4. The chemical reactions involved in the present systems first takes place at the interface between NH_4^+ and Nd^{3+} adsorption bands. When (NH_4) n-Ligand reached the rear boundary of Nd^{3+} adsorption band, the ligands are transferred to Nd^{3+} because of the large stability constant of the Nd-Ligand complex compared to that of ammonium ion-Ligand complex. During the moving down of the solution phase, which contains Nd-Ligand complex species through the Nd^{3+} adsorption band in the column, the isotopic exchange reaction takes place between Nd^{3+} ions in the resin phase and Nd-Ligand complex species in the solution phase. After that the Nd-Ligand complex reaches the Cu^{2+} ion band, where ligand are transferred to Cu^{2+} ions and Nd^{3+} ions are adsorbed in the resin phase. The related

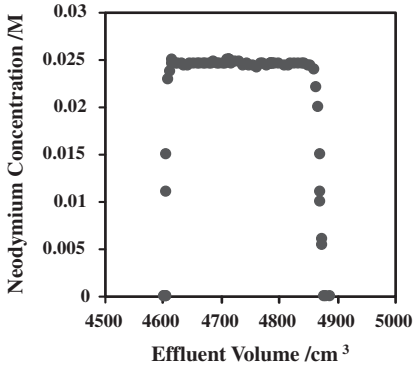

Fig. 2 The chromatogram for Nd-glycolate exchange system studied at 25 °C.

Table 2 Natural isotopic abundance of Nd.

Nd isotope	^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	^{150}Nd
Natural abundance	27.1	12.2	23.8	8.3	17.2	5.8	5.6

chemical reactions for the three types of carboxylic acids, mono-basic (glycolate), di-basic (malate) and tri-basic (citrate) ligands can be expressed, in the simplest form, as:

For the mono-basic glycolate ligand

$$4NH_4 - L_g + \underline{Nd^{3+}} + H^+ \rightarrow 4\underline{NH_4^+} + Nd - (L_g)_4 - H \quad (1)$$

$$^{H}\underline{Nd^{3+}} + {}^{L}Nd - (L_g)_4 - H \leftrightarrow {}^{L}\underline{Nd^{3+}} + {}^{H}Nd - (L_g)_4 - H \quad (2)$$

$$Nd - (L_g)_4 - H + \underline{Cu^{2+}} + H^+ \rightarrow \underline{Nd^{3+}} + Cu - (L_g)_4 - 2H \quad (3)$$

For the DI-basic malate ligand:

$$2(NH_4)_2 - L_m + \underline{Nd^{3+}} + H^+ \rightarrow 4\underline{NH_4^+} + Nd - (L_m)_2 - H \quad (4)$$

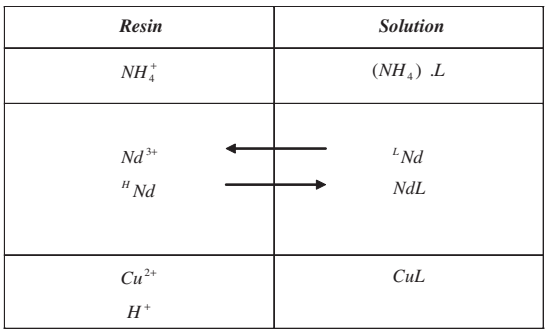

Fig. 4 Schematic diagram of the ion exchange mechanism.

$$^{H}\underline{Nd^{3+}} + {}^{L}Nd - (L_m)_2 - H \leftrightarrow {}^{L}\underline{Nd^{3+}} + {}^{H}Nd - (L_m)_2 - H \quad (5)$$

$$Nd - (L_m)_2 - H + \underline{Cu^{2+}} + H^+ \rightarrow \underline{Nd^{3+}} + Cu - (L_m)_2 - 2H \quad (6)$$

For the tri-basic citrate system:

$$(NH_4)_3 - L_c + \underline{Nd^{3+}} + H^+ \rightarrow 3\underline{NH_4^+} + Nd - L_c - H \quad (7)$$

$$^{H}\underline{Nd^{3+}} + {}^{L}Nd - L_c - H \leftrightarrow {}^{L}\underline{Nd^{3+}} + {}^{H}Nd - L_c - H \quad (8)$$

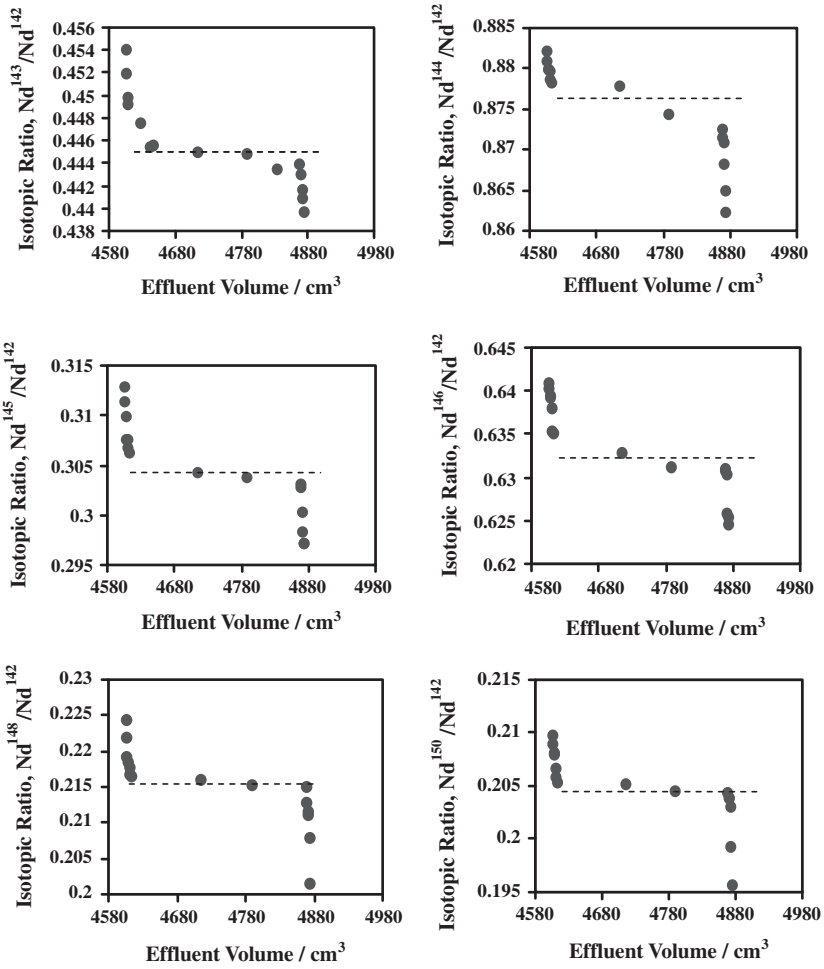

Fig. 3 Isotopic distribution of different Nd isotopes against ^{142}Nd in Nd-glycolate system at 25 °C.

$$\mathrm{Nd} - L_c - \mathrm{H} + \underline{\mathrm{Cu}}^{2+} + \mathrm{H}^{+} \rightarrow \underline{\mathrm{Nd}}^{3+} + \mathrm{Cu} - L_c - 2\mathrm{H} \quad (9)$$

where the underlines represent the species in the resin phase, L represents the ligand species (where L_g = glycolate, L_m = malate and L_c = citrate) and ^{H}Nd and ^{L}Nd represent the heavy and the light neodymium isotopes, respectively. In fact, the chemistry of the system may be more complicated than that represented by the above equations. The exact complex structure and the different possibilities of Nd and/or H_2O hydrolysis are out of the scope of the present work.

The single stage separation factor, $\alpha = (1 + \varepsilon)$ for each Nd isotopes is defined here as:

$$\alpha = 1 + \varepsilon = \left(^{142}\underline{\mathrm{Nd}}/^{H}\underline{\mathrm{Nd}}\right)/\left(^{142}\mathrm{Nd}/^{H}\mathrm{Nd}\right) \quad (10)$$

where the underline represents the species in the resin phase and H can take the values 143, 144, 145, 146, 148 and 150. The separation coefficients, ε's were calculated by using the isotopic enrichment curves of the front and rear boundaries according to the equation developed by Spedding et al. [24] and Kakihana and Kanzaki [25].

$$\varepsilon = \sum q_i |r_i - r_o| / \{Q r_o (1 - r_o)\} \quad (11)$$

where q is the amount of neodymium in the sample fraction, Q is the total amount of sorbed neodymium in the column packed resin, r_i is the isotopic ratio of ^{n}Nd/^{142}Nd, and the subscripts i and o denoted the fraction number and the original feed, respectively. In general, the isotope exchange reaction effectively proceeds and reaches the equilibrium between two phases of the solution and the resin at lower flow rate condition. In such a case, effective isotope accumulation is expected.

The mathematical averages of the two separation coefficient values obtained from the front and rear boundaries were taken to calculate the process separation coefficient (ε). The average values of the separation coefficients of each isotope relative to ^{142}Nd for different ligands are given in Table 3 with an estimated error factor of $\pm 5.0\%$. From the data shown in Table 3 it can be easily noticed that the separation coefficient increases with the increase of the mass number. This trend agrees with the previous findings in case of U [15,23], Zn [19–21], Gd [2] Nd citrate system [10] and Nd malate system [11]. The arrangement of the ligands takes the following direction with respect to the increasing capacity of each ligand to increase the separation coefficient of each isotope:

Malate ligand > Citrate ligand > Glycolate ligand

The values of the separation coefficients were plotted as a function of the mass number at 25 °C as shown in Fig. 5. A linear relationship was obtained between the mass number and the separation coefficient for the three ligands. The current discussion cannot be extended to the odd–even or mass anomaly phenomena due to the short migration of the bands that leads to high errors in the isotope ratio measurements carried out by ICP mass. The odd–even and mass anomaly phenomena were discussed for neodymium malate system elsewhere [9].

Fig. 6 shows the structure of the three ligands compared in this study according to wikipedia site. The malate structure has up to 4 possible active sites for complexion with Nd ions. This number is reduced to three only in case of citrate, as two sites were not available for complexion due to steric hindering. Glycolate has only one possible site for complexion with Nd. The number of possible complexion sits of the three ligands takes the order Malate > Citrate > Glycolate, which agree with the order of isotope effects of the three systems as studied by the separation coefficients shown above.

The plate height, HETP, is a very important factor in determining the performance of any chromatographic separation system. The smaller the value of HETP, the shorter the migration length needed for a specific separation task i.e. the higher the efficiency of the system. The value of HETP can be calculated from Eqs. (12) and (13).

$$\mathrm{HETP} = (\varepsilon/\theta_s) + (1/\theta_s^2 L) \quad (12)$$

where L is the total migration length and θ_s is the slope of the plots of ln $(r_i - r_o)$ vs. $X_i - L$ [26], where r_i is the neodymium isotopic ratio of ^{n}Nd/^{142}Nd in the fraction, r_o is the neodymium isotopic ratio of the feed solution, X_i is the hypothetical distance of the sample fraction, calculated from the starting point at the time when the boundary is eluted from the column after migration distance of L. The hypothetical distance is calculated based on the effluent volume being proportional to the migration distance of the absorbed band:

$$X_i = (V_i/Q_T) * L \quad (13)$$

where V_i is the effluent volume of the sample fraction i, Q_T is the total effluent volume and L is the total migration length. A sample of the plots of ln $(r_i - r_o)$vs. $X_i - L$ carried out at 25 °C for ^{143}Nd at Nd-malate system was shown in a previous article [11]. The values of the HETP for each neodymium isotope for different ligands at constant temperature 25 °C have been calculated using Eq. (12) and given in Table 4. It can be easily noticed from Table 4 that the values of the (HETP) are small, which leads to a higher degree of separation and a better separation performance. The HETP values of neodymium isotope separation by ion exchange chromatography in ligand exchange system are of the same magnitude of HETP values of europium isotope separation, while it is 10 times larger than those of copper. This could be due to the larger size of the ions of the f electron element like Eu and Nd compared to Cu ions [10].

Conclusions

The isotope effects of neodymium in Nd-glycolate ligand exchange system were studied by using ion exchange chromatography. The heavier isotopes ^{H}Nd were clearly found to be enriched in the Nd-glycolate species in the solution phase. The degree of fractionation takes the order, $^{143}\mathrm{Nd} \leqslant {}^{144}\mathrm{Nd} \leqslant {}^{145}\mathrm{Nd} \leqslant {}^{146}\mathrm{Nd} \leqslant {}^{148}\mathrm{Nd} \leqslant {}^{150}\mathrm{Nd}$. The separation coefficients of neodymium isotopes, ε's, were calculated from the observed isotopic ratios at the front and rear boundaries of the neodymium adsorption band. The separation coefficients of neodymium isotopes, ε's, for the Nd-glycolate ligand exchange system were compared with those of Nd-malate and Nd-citrate, which indicated that the isotope effects of neodymium as studied by the three ligands takes the following direction Malate > Citrate > Glycolate. This order agrees with the number of available sites for complexation of each ligand. The plate height, HETP, values of Nd in Nd-ligand exchange

Table 3 Average values of the separation coefficients of each Nd isotope for different ligands.

Ligand	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	^{150}Nd
Malate	2.62E−05	5.01E−05	7.55E−05	12.1E−05	14.4E−05	18.2E−05
Citrate	2.37E−05	4.58E−05	5.38E−05	6.93E−05	9.01E−05	16.2E−05
Glycolate	0.718E−05	0.793E−05	0.986E−05	1.12E−05	1.36E−05	1.49E−05

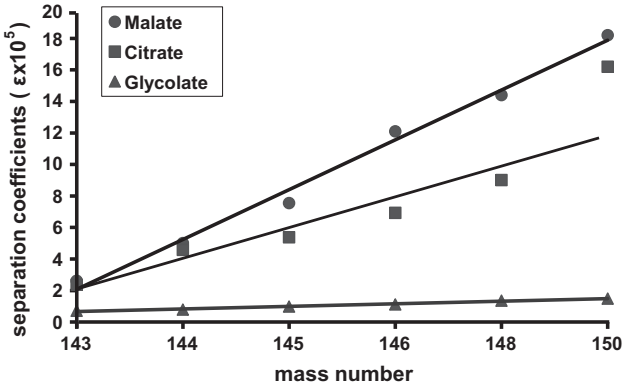

Fig. 5 Separation coefficients (ε) against the mass numbers of Nd isotopes.

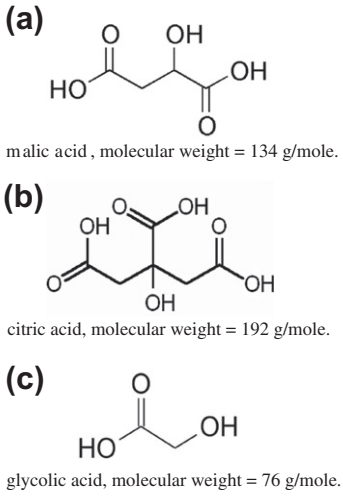

Fig. 6 Structure of the three ligands Citrate, Malate and Glycolate.

Table 4 Plate height, cm, for different ligand – Neodymium systems at 25 °C.

Ligand	Plate height					
	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	^{150}Nd
Malate	0.29	0.47	0.41	0.51	0.35	0.46
Citrate	0.76	0.22	0.13	0.25	0.15	0.39
Glycolate	0.24	0.74	0.55	0.12	0.24	0.41

systems were calculated and found to be of the same magnitude of Eu, while it is 10 times larger than Cu.

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